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TERNARY SOLID PHASE EQUILIBRIA IN THE SYSTEMS (Ag,In,Au)-(Cd,He)-Te

by

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The ternary phase diagrams of the Ag-Cd-Te, In-Cd-Te, Au-Cd-Te, Ag-Hg-Te, In-Hg-Te, and Au-Hg-Te systems were determined using x-ray powder diffraction and existing thermochemical data. In closed thermodynamic systems Ag,In, and Au were shown to be stable with respect to stoichiometric CdTe and Ag, In reactive towards stoichiometric HgTe.

The results clearly show the high chemical reactivity of metals studied with HgTe is due to the high solid phase vapor pressure of the group two element, Hg, and the thermochemical stabilities of metal-tellurium compounds. The findings of the work support the importance of thermochemical data for the prediction of stable, metallic solid phases in ternary systems and that current contacting technology may severely limit the use of HgTe in electronic devices.

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Ternary Solid Phase Equilibria in the Systems (Ag, In, Au) - (Cd, Hg) - Te

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Knowledge of the behavior of thin films on compound semiconductors has taken on increasing importance as the advantages of opto-electronic devices based on compound semiconductor technology become apparent. The chemistry of the metal-semiconductor interface ultimately controls the nature of Schottky barrier and ohmic contact formation.[1,2] Ternary phase diagrams and thermochemical data can provide useful insight towards the understanding of the chemical behavior of open-system contacts.[3,4] The two compound semiconductors examined in this work, CdTe and HgTe, are widely used in long wavelength detectors despite the difficulty in achieving stable contacts to the semiconducting material. We have begun to map the Ag, Au, In-CdTe and Ag, In, Au-HgTe ternary phase diagrams in order to gain a better appreciation of the basic chemical limitations of these materials systems.

Panchuk,[5,6] Grystiv,[7] and Tai[8] have previously investigated the solid phase equibria of the Ag, In, Au-cadmium telluride systems. The intention here is not to map the phase diagrams in great detail, but rather to determine what metallic phases are stable in contact with the stoichiometric II-VI semiconductors, see if any general pattern may be observed, and use this information to better understand and design thin metal films on compound semiconductor substrates.

The determination of the ternary phase diagrams requires knowledge of the binary systems that border each ternary diagram, evaluation of existing thermochemical data, and experimental identification of stable bulk phases for certain compositions within

the six ternary systems. Thermodynamic calculations were performed using the data collected in Table I to see if the metals Ag, In, and Au were reactive with respect to CdTe and HgTe in order to determine if a tie-line connects the elemental metal to the compound semiconductor in each of the six ternary phase diagrams.

The calculations predict that the Ag, In, Au-CdTe and Au-HgTe closed systems are pseudobinary. The Gibbs free energies of reaction, ΔG, were calculated at room temperature considering the formation of intermetallic compounds and the presence of vapor phase species at equilibrium partial pressures. Such calculations may contain substantial errors as a result of uncertainties contained in the reported values of the thermochemical data, which may be on the order of ± 3 kcal per reaction. In order to confirm the predictions of the calculations, and thus validate the thermochemical data, experiments were performed to determine the actual existence of the predicted tielines.

The experimental procedure was largely the same as Tsai,[3] with the exception that the samples were often on the order of 0.5g or less. The sample materials were sealed in fused silica tubes under 10^{-2} Torr and heated to temperatures as high as 900 ^{o}C. The products of these solid state reactions were determined by x-ray powder diffraction. Identification of resultant compounds was by JCPDS powder diffraction data[14] and by comparison with diffraction data collected from reference intermetallic compounds synthesized for this purpose.

The experimental results confirmed the thermochemical predictions in all cases. The four systems Ag, In, Au-CdTe and

Au-HgTe are essentially pseudobinary, although there is appreciable solid solubility of the group II element in the metal for these cases. The In-compound semiconductor systems are somewhat complex since they contain an invariant point due the the existence of the ternary defect compounds $HgIn_2Te_4$ and $CdIn_2Te_4$.[15] The complete phase diagrams for these systems have not yet been determined. The In-HgTe ternary is further complicated by the existence of a liquid phase at 298K for the In_xHg_{1-x} binary system for $0.0 \leq x \leq 0.88$. The results of our reaction studies indicate this liquidus region penetrates quite far into the In-HgTe phase diagram, thus making In an unsuitable contact metal for HgTe. In the Ag-HgTe system, the reaction $2Ag + HgTe \rightarrow Ag_2Te + Hg$ is favored which also makes Ag unsuitable as a contact metal for HgTe.

The nature of the group II constituent of the II-VI compound semiconductor and the free energy of formation of the metal-tellurides largely determine the chemical behavior of the ternary system. The metals Ag, In, Au should all make unreactive contacts to CdTe, provided that the system is essentially closed, ie. that Cd vapor is prevented from escaping. Similarly, Au appears to be the chemically most attractive choice for HgTe, although the effects of Hg solubility in Au must be examined more carefully. The availability of reliable thermochemical data provides a rapid, convenient means for evaluating possible contact materials and the results of this study indicate that the values presented in Table I can be used with reasonable confidence.

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Table I. Thermodynamic properties at 298K and 1 atm.[a]

Species	ΔH^0(kcal/mole)	S^0(cal/mole-K)	Melting Pt./K
Ag	0.0	10.20	1234
Ag_2Te	-8.6	36.7	1233[d]
Ag_5Te_3	-8.8[b]	------	693[d]
Au	0.0	11.32	1336
$AuTe_2$	-4.45	33.87	737
Cd	0.0	9.95	594
CdTe	-24.33	22.24	1364
Hg(l)	0.0	18.19	-----
HgTe	-7.6	27.	643[e]
In	0.0	13.82	429
In_2Te	-19.0	37.5	693
InTe	-17.2	25.26	968
In_2Te_3	-45.8	57.0	948
In_2Te_5	-45.8	87.0[c]	728
Te	0.0	11.88	723

a. All data from (Ref. 9) except for elemental data which is from (Ref. 10) unless indicated.
b. Estimated from data in (Ref. 11)
c. Estimated by method in (Ref. 9)
d. From (Ref. 12).
e. Decomposes under vacuum (Ref. 13).

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